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Tracking a Paternò-Büchi Reaction in Real Time using Transient Electronic and Vibrational Spectroscopies**

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***Abstract*:** *A detailed mechanistic investigation of the early stages of the Paternò-Büchi reaction following 267 nm excitation of benzaldehyde in cyclohexene has been completed using ultrafast, broadband transient UV-visible and IR absorption spectroscopies. Absorption due to electronically excited triplet state benzaldehyde decays on a 80 ps timescale via reaction with cyclohexene. The growth and subsequent decay of the biradical intermediate produced following C-O bond formation is followed by transient vibrational spectroscopy. The biradical decays by ring closure to an oxetane or by dissociating, reforming the ground state reactants. Detailed kinetic analysis allowed derivation of quantum yields and rate constants for these competing biradical decay processes,* $\phi_{oxetane} = 0.53$, $\phi_{diss} = 0.47$, $k_{oxetane} = 0.27 \pm 0.09\ ns^{-1}$ *and* $k_{diss} = 0.24 \pm 0.09\ ns^{-1}$. *This study provides a striking illustration of the ways in which contemporary ultrafast transient absorption spectroscopy methods can be used to dissect the mechanism and kinetics of a classic photo-reaction.*

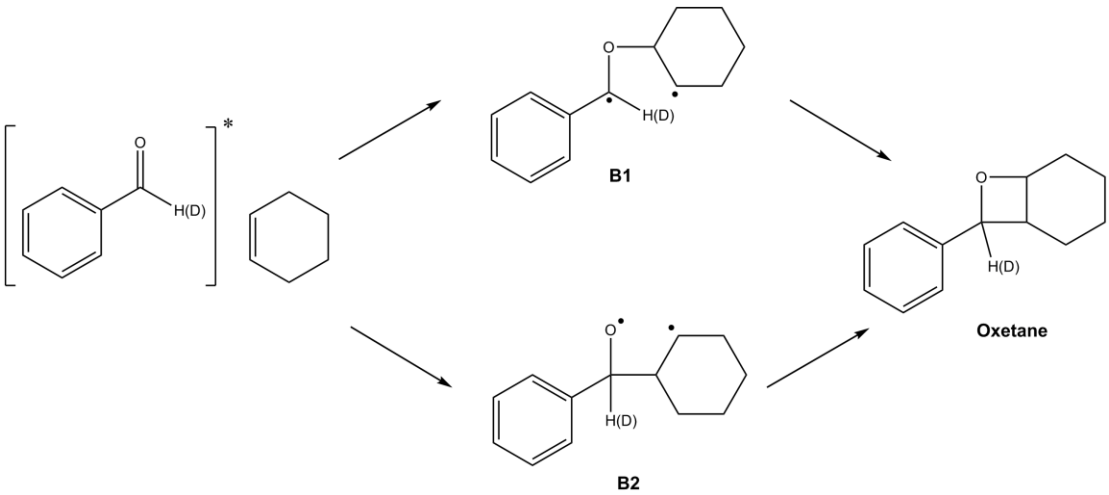
Keywords: photochemistry, photo-cycloaddtion, kinetics, time-resolved

Introduction

The last few years have witnessed a resurgence of interest in organic photochemistry, and its application in synthesis in both academia and industry.[1–3] The Paternò-Büchi (PB) reaction, a [2+2] photocycloaddition between an electronically excited carbonyl compound and an alkene to yield an oxetane, is one such example. First described by Paternò,[4] the reaction attracted renewed interest following the mechanistic studies of Büchi *et al.* which showed that the reaction proceeded *via* a 1,4-biradical intermediate.[5] Since these initial works, numerous studies have been devoted to exploring mechanistic details of several PB reactions with differing substrates.[6–17] Reaction between the carbonyl and the alkene can proceed by attack at either the C or the O atom of the carbonyl group, forming one of two possible biradical intermediates. Which is formed is dependent on their relative stabilities,[18] and determines the regioselectivity of the resulting products. An earlier picosecond pump-probe study of the PB reaction of benzophenone and dioxene confirmed the step-wise nature of the reaction by observation of the biradical intermediate created by C–C bond formation.[9,19] The nanosecond lifetime of this intermediate was also noted

and used to identify that a triplet state biradical had been formed which subsequently underwent intersystem crossing to form the final singlet oxetane product. The reaction now finds widespread use in synthetic chemistry as a means of adding high-level functionality in one preparative step.[1,20]

The present study explores a prototypical PB reaction between benzaldehyde and cyclohexene (scheme 1) following photoexcitation at 267 nm, which could proceed *via* one of two biradicals: B1, obtained by C–O bond formation, or B2, a biradical from C–C bond formation. Either biradical could then ring close to form the final oxetane product. The substrates chosen for this particular proving study were selected on the basis of operational simplicity (having the alkene serve as the solvent also simplifies the kinetic analysis) and their absorptive properties (benzaldehyde because of its UV absorption at the 267 nm pump wavelength and its strong and characteristic IR absorptions, and cyclohexene for its UV transparency at 267 nm and its limited IR absorption features in the probe regions of interest).



Scheme 1 – Possible intermediates and products in the Paternò-Büchi reaction between benzaldehyde-(d_1) and cyclohexene.

The progress of this reaction is investigated in real time using transient broadband electronic and/or vibrational absorption spectroscopies (TEA and TVA, respectively) – two complementary techniques that are finding increasing use in exploring the intimate dynamics of both photodissociation and bimolecular reactions in solution.[21–24] The present study has two aims: to gain new and direct insight into this important reaction (extracting quantum yields of intermediate and product formation wherever possible) and to illustrate the role of contemporary ultrafast transient absorption spectroscopy methods in unravelling mechanistic details of a classic photoinduced organic reaction.

Experimental

The TEA and TVA spectra were recorded using the ULTRA laser facility at the STFC Rutherford Appleton Laboratory.[25] An amplified titanium sapphire laser system generated 800 nm (band center) pulses with 50 fs pulse duration at a 10 kHz repetition rate. The broadband UV/visible probe was generated by focusing a portion of the 800 nm radiation into a CaF_2 disc which was rastered in the plane orthogonal to the beam propagation axis. A further portion of the 800 nm light was used to pump an optical parametric amplifier to produce mid-IR pulses with a bandwidth of ~500 cm^{-1}. In each experiment, the pump and probe pulses were overlapped in the sample with their respective linear polarization vectors aligned at the magic angle, before the transmitted radiation was dispersed by a grating onto a 512 element silicon array (for UV/visible detection) or a 128 element HgCdTe array (for IR detection). The samples were flowed continuously through a Harrick cell with a 100 μm PTFE spacer between CaF_2 windows at a concentration chosen to ensure an absorbance of 0.5 at 267 nm (40 mM benzaldehyde or benzaldehyde-d_1) as described previously.[26] Benzaldehyde (99%), and benzaldehyde-d_1 (98 atom % D), and cyclohexene were obtained from Sigma-Aldrich and used without further purification.

Results

Figure 1 shows a selection of TEA spectra across the wavelength range 345-610 nm recorded following 267 nm photoexcitation of a 40 mM solution of benzaldehyde in cyclohexene at pump-probe delays between 2 ps and 2 ns. Absorption is evident at all wavelengths in spectra measured at the shortest of the displayed pump-probe delays (δt = 2 ps) and decays with a common timescale. Differences in the early time ($\delta t \leq 5$ ps) decay of the absorption at ~350 nm might indicate some contribution from another (short lived) species or simply be indicative of vibrational cooling. Numerical integration of these spectra between 370 and 600 nm allows the transient population change of this absorption to be monitored; this time evolving amplitude is shown in fig. 3.

Figures 2(a), (b) and (c) show selected TVA spectra obtained in the respective probe ranges 1390-1660 cm^{-1}, 1670-1780 cm^{-1} and 2200-2360 cm^{-1} following 267 nm excitation of a 40 mM solution of benzaldehyde-d_1 in cyclohexene at various pump-probe delays in the range 2 ps $\leq \delta t \leq$ 2.5 ns. Benzaldehyde-d_1 was used in the TVA experiments to allow observation of C–D vibrations in this reagent, and in any reaction intermediates and products, free from overlapping solvent bands. The spectra in fig. 2(a) show four features of note. Two, at ~1447 cm^{-1} and ~1655 cm^{-1}, are due to the cyclohexene solvent and are not considered further. The negative-going doublet centred at 1597 cm^{-1} reflects the depletion of the benzaldehyde-d_1 ground (S_0) state population by the 267 nm pump pulse as does the 1690 cm^{-1} feature in fig. 2(b). The fourth feature, at 1404 cm^{-1}, is absent at short δt, maximises at δt ~150 ps and then decays on a nanosecond timescale. A very weak absorption feature at ~2257 cm^{-1} (fig. 2(c)) shows a similar time evolution. Figure 3 shows the

time dependent amplitudes of the 1690 cm^{-1} S_0 depletion feature and of the 1404 and 2257 cm^{-1} gain signals, along with the corresponding fits to a kinetic model described later. The incomplete recovery of the parent bleach signal within the observation time window (δt = 2.5 ns) is of particular note; the extent of this bleach recovery indicates that only a fraction of the photoexcited benzaldehyde-d_1 molecules return to the S_0 state, implying that the remainder react further to form product species.

We focus first on the electronic absorption spectra shown in fig. 1. After δt = 5 ps, the absorption across the entire probe region exhibits the same decay time constant of ~80 ps. The UV photophysics of benzaldehyde has been investigated extensively;[27–30] the consensus view is that initial photoexcitation to the first excited singlet (S_1) state leads to rapid (~100 fs timescale) intersystem crossing (ISC) to either (or both of) the first (T_1) or second (T_2) triplet excited states.[29] Neither of the possible biradicals nor the oxetane shown in scheme 1 are expected to absorb across the whole 345-630 nm range. The observed TEA signals are thus attributed to excited state absorption by benzaldehyde molecules in their T_1 (and possibly T_2) states.

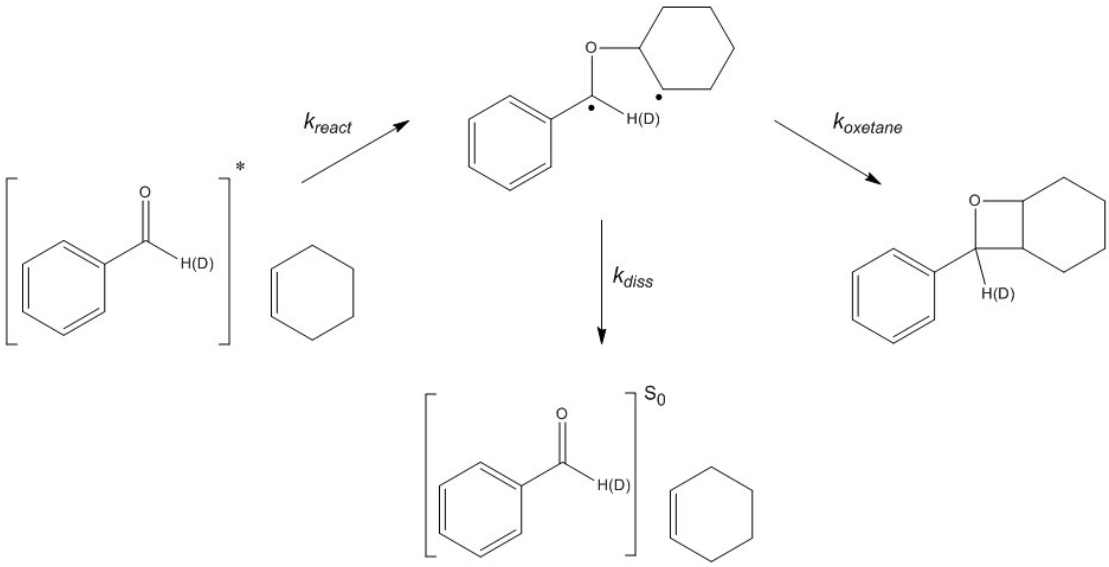
Four transient features have been identified in the TVA spectra. The doublet bleach signal centred at 1597 cm^{-1} and bleach feature at 1690 cm^{-1} are readily assigned to benzaldehyde-d_1 molecules in the S_0 state (see Table S1 in the electronic supplementary information (ESI)). The transient absorptions at 1404 and 2257 cm^{-1} show very similar time dependences (fig. 3), suggesting that both are signatures of a common species. Their kinetic behaviour (*i.e*. a fast rise followed by a slower decay) is characteristic of a reactive intermediate formed *via* reaction involving photoexcited benzaldehyde. Comparison with the kinetic behaviour observed in prior literature relating to PB reactions [6–17,19] suggests that these absorptions are signatures of the biradical intermediate(s) formed by reaction between benzaldehyde(T_1) and cyclohexene. Once formed, this biradical would be expected to either undergo intersystem crossing prior to ring-closure (to form the final oxetane), or dissociation to reform benzaldehyde in its S_0 state, it is not clear from these measurements whether ISC occurs before or after dissociation has occurred.

The observed absorptions allow distinction between biradicals B1 and B2. Reference to the harmonic normal mode wavenumbers and associated fundamental band intensities for the T_1 states of both biradicals (calculated using the Gaussian 09 computer package [31] and listed in Table S2 (ESI)) encourages assignment of both the 1404 and 2257 cm^{-1} features to intermediate B1 (c.f the calculated values of 2344 cm^{-1} and 2162 cm^{-1} for the C-D stretching modes of B1 and B2 respectively). B1 is also predicted to be ~50 kJ mol^{-1} more stable than biradical B2 (calculated relative energies using Gaussian 09/DFT/B3LYP/6-311g). B2 is not predicted to have any particularly strong IR absorption features in the probe ranges of current interest (see Table S1), and none are observed. Thus all we can assert with confidence is that the absorption features for

which kinetic data have been obtained are associated with the B1 biradical, as expected from its greater stability relative to the B2 biradical.

Discussion

The experimental results and assignments encourage development of the kinetic model shown in Scheme 2.



Scheme 2 – Kinetic scheme consistent with the observed experimental results

The cyclohexene solvent is in large excess, so the kinetics of its reaction with benzaldehyde(T_1) can be treated as pseudo-first order and the necessary rate equations solved analytically (equations (1) to (4)). [32]

$$[Benzaldehyde(T_n)](t) = y_0 + e^{-k_{react}t} \tag{1}$$

$$[C-O\ Biradical](t) = y_0 + \frac{k_{react}}{-k_{react}+k_{oxetane}+k_{diss}}\left(e^{-k_{react}t} + e^{-(k_{oxetane}+k_{diss})t}\right) \tag{2}$$

$$[Oxetane](t) = y_0 + \frac{k_{oxetane}}{k_{oxetane}+k_{diss}} - \frac{k_{oxetane}e^{-k_{react}t}}{-k_{react}+k_{oxetane}+k_{diss}} + \frac{k_{react}k_{oxetane}e^{-(k_{oxetane}+k_{diss})t}}{(k_{oxetane}+k_{diss})(-k_{react}+k_{oxetane}+k_{diss})} \tag{3}$$

$$[Benzaldehyde(S_0)](t) = y_0 + \frac{k_{diss}}{k_{oxetane} + k_{diss}} - \frac{k_{diss} e^{-k_{react} t}}{-k_{react} + k_{oxetane} + k_{diss}} + \frac{k_{react} k_{oxetane} e^{-(k_{oxetane} + k_{diss})t}}{(k_{oxetane} + k_{diss})(-k_{react} + k_{oxetane} + k_{diss})} \quad (4)$$

Three of the four time-dependent populations implicated in the kinetic model are monitored in the present study – benzaldehyde(T_1), *via* TEA (fig. 1), and B1 and benzaldehyde(S_0) populations, *via* TVA (figs. 2(a), (b) and (c)). No spectral signature of the oxetane product was identified in this work, but a value for its formation rate coefficient, $k_{oxetane}$, can still be extracted from the kinetic fits since the decay of B1, the formation of the oxetane product and the recovery of the S_0 parent are all controlled by an *effective* rate coefficient, $k_{obs} = k_{oxetane} + k_{diss}$. Further, the asymptotic magnitude of the bleach recovery provides a direct measure of the dissociation quantum yield, ϕ_{diss}. Individual values for k_{diss} and $k_{oxetane}$ can thus be extracted from the relation

$$\phi_{diss} = \frac{k_{diss}}{k_{diss} + k_{oxetane}} = \frac{k_{diss}}{k_{obs}} \quad (5)$$

The fits to the above kinetic scheme are shown in fig 3, and the rate coefficients so derived are listed in Table 1.

Table 1 - Kinetic parameters for the PB reaction of benzaldehyde-d_1 and cyclohexene.

k_{react} / ns^{-1}	12 ± 1
k_{obs} / ns^{-1}	0.51 ± 0.07
k_{diss} / ns^{-1}	0.24 ± 0.09
$k_{oxetane}$ / ns^{-1}	0.27 ± 0.09
ϕ_{diss}	0.47 ± 0.1
$\phi_{oxetane}$	0.53 ± 0.1

We emphasise that the TEA data and associated kinetics are obtained from a solution containing non-deuterated benzaldehyde while the TVA experiments used the mono-deuterated equivalent. Griesbeck *et al.*[14] have explored kinetic isotope effects in the PB reaction between benzaldehyde and 2,3-dihydrofuran and found a marked increase in diastereoselectivity upon mono-deuteration, which they attributed to a change in the lifetime of the 1,4-biradical. The present TEA measurements only yield a lifetime for the electronically excited benzaldehyde molecules, which

matches the rate of biradical build-up obtained from analysis of the TVA data involving benzaldehyde-d_1. In order to ensure that the present analysis is immune to any similar change in biradical lifetime, the reported kinetics are derived entirely from the TVA data.

The quoted errors on k_{react} , k_{obs} and ϕ_{diss} in Table 1 are 1σ standard deviations from fitting TVA data (as in fig. 3) in terms of scheme 2. The full extent of the parent bleach recovery occurs after the long time limit of the observations; the present fitting yields an asymptotic value ϕ_{diss} = 0.47, implying a quantum yield for ring-closure to form the oxetane, $\phi_{oxetane}$, of 0.53. The present data thus imply a small preference for oxetane formation (rather than dissociation to reform benzaldehyde and cyclohexene) in this particular PB reaction, but it would surely be rewarding to extend this exploratory study to the kinetic and selectivity effects of temperature and solvent, and how this finding extrapolates to other reactant pairs. Ring-closure (*i.e*. oxetane formation) must involve the singlet biradical, formed by ISC from its triplet precursor. Dissociation (*i.e*. reforming the reactants), in contrast, can be envisaged to occur from either (or both) the singlet and triplet states of the biradical. The energy separation of these two states would be expected to be conformationally dependent, and to fall to near zero when the radical sites are well separated. There is still much to explore about the detailed dynamical factors that influence (and determine) the branching between ring-closure and dissociation of the biradical intermediate [10] and, as this report shows, ultrafast transient absorption spectroscopies could be an important tool in advancing such understanding.

Conclusion

Broadband transient electronic and vibrational absorption spectroscopies have been used to follow and characterise the 267 nm photoinititated Paternò-Büchi reaction between benzaldehyde and cyclohexene. TEA reveals absorption of a triplet state (almost certainly the T_1 state) of benzaldehyde that decays on a 80 ps timescale through reaction with cyclohexene, while TVA spectroscopy allows us to track the growth, and subsequent decay, of the triplet biradical (B1) that results following C–O bond formation. B1 decays in two ways – by ring-closing, yielding the oxetane product, or by dissociating, to reform the benzaldehyde(S_0) and cyclohexene reactants. The quantum yields for these respective processes are determined as: ϕ_{oxetane} = 0.53 and ϕ_{diss} = 0.47, with corresponding rate constants of 0.27 ± 0.09 ns^{-1} and 0.24 ± 0.09 ns^{-1}. The study illustrates the potential of transient absorption spectroscopy methods for providing quantitative mechanistic insight into one particular photoinititated reaction, but also serves to highlight the applicability of such methods for probing the intimate dynamics of many other classic organic photo-reactions. This work also complements previous isolated molecule studies [17] and state-of-the-art theoretical treatments [33] of the PB reaction which investigated the role of the nature of the excited state has upon the outcome of the reaction.

ASSOCIATED CONTENT

Harmonic and anharmonic vibrational wavenumbers of benzaldehyde-$d_1(S_0)$ calculated using Gaussian 09 at the DFT/B3LYP/6-311g level of theory. Harmonic vibrational wavenumbers of the lowest triplet states of the biradical structures B1 and B2 calculated using Gaussian 09 at DFT/UB3LYP/6-311g level of theory. This information is available free of charge via the Internet at http://pubs.acs.org

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Figures

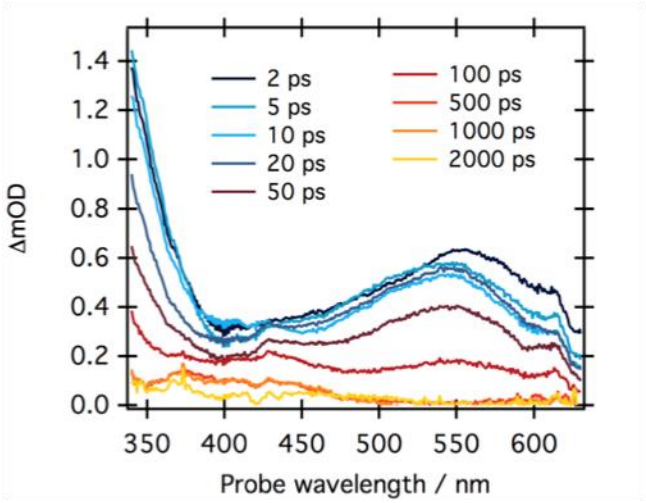

Figure 1

TEA spectra of 40 mM benzaldehyde in cyclohexene following 267 nm photoexcitation, measured in the 345-610 nm range at different pump-probe time delays.

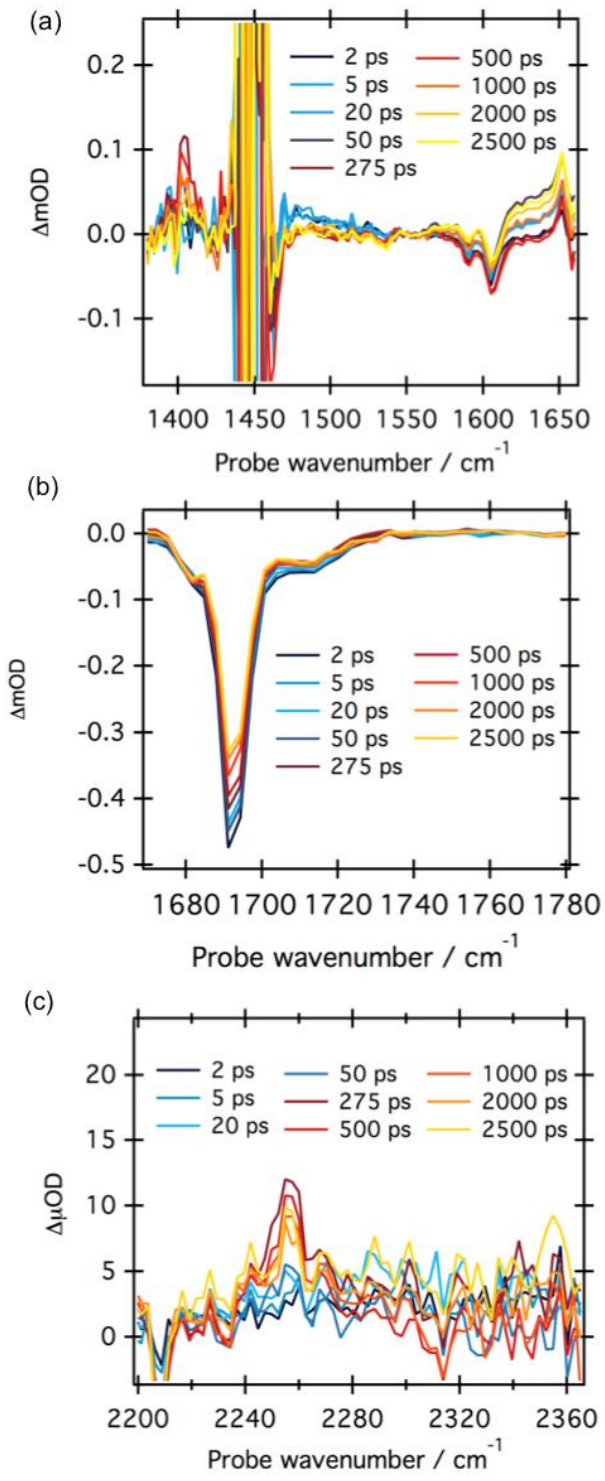

Figure 2

TVA spectra of 40 mM benzaldehyde-d_1 in cyclohexene following 267 nm photoexcitation, measured in the wavenumber ranges (a) 1390-1660 cm^{-1} (b) 1670-1780 cm^{-1} and (c) 2200-2360 cm^{-1} at various pump-probe delays.

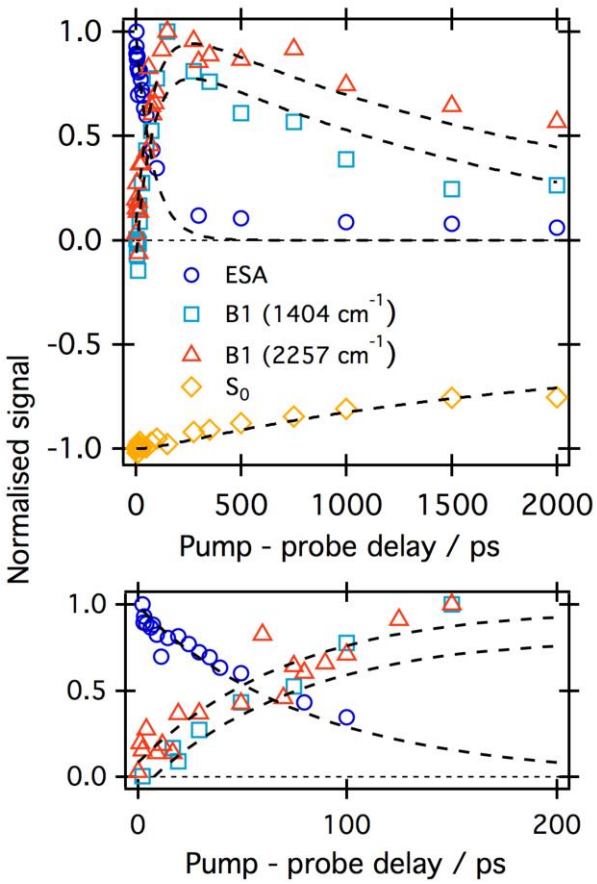

Figure 3

Plots showing the time varying normalized amplitudes of spectral features associated with the excited state absorption of benzaldehyde (ESA, 370-600 nm), biradical B1 (at 1404 cm^{-1} and at 2257 cm^{-1}) and benzaldehyde-$d_1(S_0)$ (at 1690 cm^{-1}), along with best kinetic fits (dashed lines) to these data in terms of eqs. (1), (2) and (4). The lowest panel displays the early time data on an expanded time scale.

References

(1) Hoffmann, N. Photochemical Reactions as Key Steps in Organic Synthesis. *Chem. Rev.* **2008**, *108*, 1052–1103.

(2) Knowles, J. P.; Elliott, L. D.; Booker-Milburn, K. I. Flow Photochemistry: Old Light through New Windows. *Beilstein J. Org. Chem.* **2012**, *8*, 2025–2052.

(3) Bach, T.; Hehn, J. P. Photochemical Reactions as Key Steps in Natural Product Synthesis. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 1000–1045.

(4) Paterno, E.; Chieffi, G. No Title. *Gazz. Chim. Ital.* **1909**, *39*, 341–361.

(5) Buchi, G.; Inman, C. G.; Lipinsky, E. S. Light-Catalyzed Organic Reactions. I. The Reaction of Carbonyl Compounds with 2-Methyl-2-Butene in the Presence of Ultraviolet Light. *J. Am. Chem. Soc.* **1954**, *76*, 4327–4331.

(6) Yang, N. C.; Loeschen, R.; Mitchell, D. On the Mechanism of the Paterno-Buchi Reaction. *J. Am. Chem. Soc.* **1967**, *89*, 5465–5466.

(7) Farid, S.; Hartman, S. E.; DeBoer, C. D. Reversible Energy Transfer and Oxetane Formation in the Photoreactions of Carbonyl Compounds with Benzofurans. *J. Am. Chem. Soc.* **1975**, *97*, 808–812.

(8) Caldwell, R. A.; Majima, T.; Pac, C. Some Structural Effects on Triplet Biradical Lifetimes. Norrish II and Paterno-Buchi Biradical. *J. Am. Chem. Soc.* **1982**, *104*, 629–630.

(9) Freilich, S. C.; Peters, K. S. Picosecond Dynamics of the Paterno-Buchi Reaction. *J. Am. Chem. Soc.* **1985**, *107*, 3819–3822.

(10) Griesbeck, A. G.; Mauder, H.; Stadtmuller, S. Intersystem Crossing in Triplet 1 , 4-Biradicals : Conformational Memory Effects on the Stereoselectivity of Photocycloaddition Such as Transient Spectroscopy in Solution or in Matrix. *Acc. Chem. Res.* **1994**, *27*, 70–75.

(11) Palmer, I. J.; Ragazos, I. N.; Bernardi, F.; Olivucci, M.; Robb, M. A. An MC-SCF Study of the (Photochemical) Paterno-Buchi Reaction. *J. Am. Chem. Soc.* **1994**, *116*, 2121–2132.

(12) Griesbeck, A. G.; Buhr, S.; Fiege, M.; Schmickler, H.; Lex, J. Stereoselectivity of Triplet Photocycloadditions : 1 Diene - Carbonyl Reactions and Solvent Effects Triplet Excited Component Are Mostly Conducted via Triplet. *J. Org. Chem.* **1998**, *63*, 3847–3854.

(13) Kutateladze, A. G. Conformational Analysis of Singlet-Triplet State Mixing in Paterno. *J. Am. Chem. Soc.* **2001**, *123*, 9279–9282.

(14) Griesbeck, A. G.; Bondock, S.; Cygon, P. Substantial (2)h-Magnetic Isotope Effects on the Diastereoselectivity of Triplet Photocycloaddition Reactions. *J. Am. Chem. Soc.* **2003**, *125*, 9016–9017.

(15) D'Auria, M.; Emanuele, L.; Racioppi, R. Regio- and Stereoselectivity in the Paternò-Büchi Reaction on Furan Derivatives. *Int. J. Photoenergy* **2006**, *2006*, 1–11.

(16) D'Auria, M.; Racioppi, R. A DFT Study of 1,4-Biradical Intermediates Involved in Stereoselective Paternò-Büchi Reactions. *European J. Org. Chem.* **2010**, *2010*, 3831–3836.

(17) Brogaard, R. Y.; Schalk, O.; Boguslavskiy, A. E.; Enright, G. D.; Hopf, H.; Raev, V.; Tarcoveanu, E.; Sølling, T. I.; Stolow, A. The Paternò-Büchi Reaction: Importance of Triplet States in the Excited-State Reaction Pathway. *Phys. Chem. Chem. Phys.* **2012**, *1*, 8572–8580.

(18) Zimmerman, H. E. Mechanistic Organic Photochemistry. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 1–11.

(19) Freilich, S. C.; Peters, K. S. Observation of the 1,4-Biradical in the Paterno-Buchi Reaction. *J. Am. Chem. Soc.* **1981**, *103*, 6255–6257.

(20) D'Auria, M.; Racioppi, R. Oxetane Synthesis through the Paternò-Büchi Reaction. *Molecules* **2013**, *18*, 11384–11428.

(21) Harris, S. J.; Murdock, D.; Zhang, Y.; Oliver, T. A. A.; Grubb, M. P.; Orr-Ewing, A. J.; Greetham, G. M.; Clark, I. P.; Towrie, M.; Bradforth, S. E.; et al. Comparing Molecular Photofragmentation Dynamics in the Gas and Liquid Phases. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6567 – 6582.

(22) Elles, C. G.; Crim, F. F. Connecting Chemical Dynamics in Gases and Liquids. *Annu. Rev. Phys. Chem.* **2006**, *57*, 273–302.

(23) Riedle, E.; Bradler, M.; Wenninger, M.; Sailer, C. F.; Pugliesi, I. Electronic Transient Spectroscopy from the Deep UV to the NIR: Unambiguous Disentanglement of Complex Processes. *Faraday Discuss.* **2013**, *163*, 139–158.

(24) Orr-Ewing, A. J. Perspective: Bimolecular Chemical Reaction Dynamics in Liquids. *J. Chem. Phys.* **2014**, *140*, 090901 – 12.

(25) Greetham, G. M.; Burgos, P.; Cao, Q.; Clark, I. P.; Codd, P. S.; Farrow, R. C.; George, M. W.; Matousek, P.; Parker, A. W.; Pollard, M. R.; et al. Submitted Papers ULTRA : A Unique Instrument for Time-Resolved Spectroscopy. *Appl. Spectrosc.* **2010**, *64*, 1311–1319.

(26) Harris, S. J.; Murdock, D.; Grubb, M. P.; Greetham, G. M.; Clark, I. P.; Towrie, M.; Ashfold, M. N. R. Transient Electronic and Vibrational

Absorption Studies of the Photo-Claisen and Photo-Fries Rearrangements. *Chem. Sci.* **2014**, *5*, 707–714.

(27) Berger, M.; Goldblatt, I. L.; Steel, C. Photochemistry of Benzaldehyde. *J. Am. Chem. Soc.* **1973**, *95*, 1717–1725.

(28) Ohmori, N.; Suzuki, T.; Ito, M. Why Does Intersystem Crossing Occur in Isolated Molecules. *J. Phys. Chem.* **1988**, *92*, 1086–1093.

(29) Ou, Q.; Subotnik, J. Electronic Relaxation in Benzaldehyde Evaluated via TD-DFT and Localized Diabatization: Intersystem Crossings, Conical Intersections, and Phosphorescence. *J. Phys. Chem. C* **2013**, *117*, 19839–19849.

(30) Fang, W.-H.; Phillips, D. L. The Crucial Role of the S1/T2/T1 Intersection in the Relaxation Dynamics of Aromatic Carbonyl Compounds Upon N→π* Excitation. *ChemPhysChem* **2002**, *10*, 889–892.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennuchi, B.; Petersson, G.; et al. *Gaussian 09, Revision D.01*; Gaussian Inc.: Wallingford, CT, 2010.

(32) Berberan-Santos, M.; Martinho, J. The Integration of Kinetic Rate Equations by Matrix Methods. *J. Chem. Educ.* **1990**, *67*, 375 – 379.

(33) Maeda, S.; Taketsugu, T.; Morokuma, K. Exploring Pathways of Photoaddition Reactions by Artificial Force Induced Reaction Method: A Case Study on the Paterno-Buchi Reaction. *Z. Phys. Chem.* **2013**, *227*, 1421–1433.